

Thermodynamics of Lanthanide TMEDTA Complexation

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Abstract

The thermodynamic parameters for the formation of 1:1 metal-to-ligand complexes of 1,4-dinitrilobutane, N,N,N',N' -tetraacetate (TMEDTA) with lanthanide cations have been determined at 25 °C and 0.50 M ($NaClO_4$) ionic strength. The enthalpy of complexation is endothermic so the stability of the complexes is due to the large, positive entropies. Arguments are presented for much weaker lanthanide–nitrogen interactions in the Ln TMEDTA complex than in the Ln EDTA, presumably due to the larger $N-Ln-N$ chelate ring of the former.

Introduction

Previously, a comparison of the thermodynamic parameters of complexation of lanthanide cations by a series of aminocarboxylate ligands [1, 2] showed that the entropy of complexation was related to the number of bonding carboxylate groups and independent of the presence of $Ln-N$ interaction. The estimated enthalpy contribution of the $Ln-N$ interaction was found to correlate with the ΣpK_a of the amino groups of the ligands. The diamino ligands studied were ethylenediaminetetraacetate (EDTA), 1,2-cyclohexyldiaminetetraacetate (DCTA), and hydroxyethylenediaminetriacetate (HEDTA). In all three, an ethylene group separated the amino groups and the carboxylates are present as acetate-type arms attached to the amino groups. Thus, the carboxylate–lanthanide–amino chelate rings as well as the amino–lanthanide–amino ones are 5-membered.

Lanthanide complexes of diamino tetracarboxylate ligands with a three carbon chain separating the nitrogens have been studied. The stability constants for the complexes with *rac*-2,4-diaminopentane- N,N,N',N' -tetraacetate [3] and 1,3-diaminopropane- N,N,N',N' -tetraacetate [4] were determined in 0.10 M (KNO_3) ionic strength solution while the enthalpy of complexation was also reported for the latter ligand [4]. In both systems, it was assumed that the ligands are hexadentate in their coordination to the lanthanides.

In the present article, we report the results of a study of the thermodynamics of lanthanide complexation with a polyaminocarboxylate ligand with a 4 carbon chain separating the amino groups, 1,4-dinitrilobutane, N,N,N',N' -tetraacetate (TMEDTA). The stability constants were determined by pH-potentiometric titration and the enthalpy values by titration calorimetry.

Experimental

Reagents and Solutions

Lanthanide stock solutions were prepared by dissolving the appropriate metal oxide (from the American Potash and Chemical Corp.) in a minimum amount of concentrated perchloric acid. The solutions were evaporated to near dryness to remove excess acid and diluted to volume with water. The lanthanide concentration was determined by titration [5] with Baker reagent grade EDTA using xylenol orange as an indicator in an acetate buffer. Calcium perchlorate was obtained as a salt from Alfa Chemicals which was dissolved and standardized [5] by EDTA titration using Erichrome Black T as an indicator in ammonia buffer (pH 10).

TMEDTA was prepared in a manner similar to that of Tanaka *et al.* [6, 7] for 1,3-diaminopropane- N,N,N',N' -tetraacetate, TMDTA (= 1,3-trimethylenediaminetetraacetate). The compound decomposed at 225 °C with no visual KCl residue while titration with sodium hydroxide indicated a purity of 99.2%. A 1H NMR spectrum of a solution was consistent with pure TMEDTA. Three peaks were observed, a broad multiplet at 1.41 ppm corresponding to the central methylenic protons of the butyl group, a broad multiplet at 2.52 ppm corresponding to the methylenic protons of the butyl group which are adjacent to the nitrogens, and a singlet at 3.15 ppm due to the protons of the (freely rotating) acetate groups. These shifts, measured on the Bruker 270 MHz spectrometer in the Florida State University NMR laboratory, are relative to the internal standard sodium 2,2-dimethyl-2-silapentane-5-sulfonate.

Potentiometry

The pH was measured with a Radiometer PHM 84 pH meter using a Radiometer combination glass electrode with saturated calomel + NaCl and an internal reference saturated Ag/AgCl system. This system was calibrated with 'BuffAR' pH 4.01, 'BuffAR' pH 7.00, 0.01 M Borax (pH 9.174 at 25 °C) and 0.01 M citric acid buffer (pH 2.624 at 25 °C). Corrections were made for the activity of the hydrogen ion from the reading of the pH of known concentrations of perchloric acid in solutions of constant ionic strength (0.50 M) using NaClO₄ as supporting electrolyte. This correction term had a value of +0.20, which is consistent with earlier reports [8].

To determine the acid association constants of TMEDTA, a 50 ml aliquot of 10⁻³ M solution of the tetraprotic acid at constant 0.50 M ionic strength (NaClO₄) was titrated with 0.1 M NaOH. The acid association constants, pK₁ and pK₂, were calculated by the method of Bjerrum [9, 10]. The temperature was maintained at 25 °C ± 0.1 °C.

To determine the stability constants of TMEDTA complexes, the pH was measured during the titration by 0.10 M NaOH of 50 ml of solution which was 10⁻³ M in total metal concentration and 10⁻³ M in total ligand concentration. The temperature was maintained at 25 ± 0.1 °C and the ionic strength at 0.50 M with NaClO₄. Due to the limited solubilities of the LnHL species of the lanthanide-TMEDTA complexes, the stability constants of the lightest lanthanides could not be determined by the direct pH potentiometric titration method.

Calorimetry

A calcium-TMEDTA solution was prepared of 0.01 M total calcium and 0.01 M total ligand (TMEDTA). The pH was adjusted to 8.5 with sodium hydroxide prior to final dilution. Stock solutions of lanthanide perchlorate were diluted to 0.01 to 0.03 M and adjusted within a pH range of 5–6 with NaOH prior to final dilution.

The titration calorimetry system used in these experiments has been described in earlier publications [11–13]. Because of precipitation of the LnHL species, direct titration of the Ln with ligand (or vice versa) was not feasible. Therefore, a competitive system was used whereby the Ln(III) competes with Ca(II) for the ligand. An initial pH of 8.5 in the Ca–L system provided a good proportion of CaL and CaHL while the CaH₂L species was negligible. By varying the pH slightly throughout the titration, satisfactory concentrations of LnL and LnHL could be maintained.

The heats of protonation of the ligand were measured by titrating TMEDTA (0.01 M, I = 0.50 M, pH 10.5) with perchloric acid (0.1 M, I = 0.50 M). The heat of formation of the CaL complex was

measured by titrating calcium perchlorate (0.1 M, I = 0.50 M, pH 9) with TMEDTA (0.1 M, I = 0.50 M, pH 10). The heat of formation of the CaHL complex was determined from knowledge of the heat of protonation of the CaL complex obtained by titrating a solution consisting of 1:1 calcium-to-ligand ratio (0.1 M, I = 0.5 M, pH = 12) with perchloric acid.

50 ml of 1:1 calcium-to-ligand (TMEDTA) solution was titrated with the lanthanide perchlorate solution in sufficient quantities to provide at least 100 mJ of heat change per addition of titrant. Heats of dilution were measured separately to obtain the values for this correction. The pH at each point in the titration was measured by a concurrent potentiometric titration.

Calculations

Mass balance equations were solved [10] with the primary potentiometric titration data to obtain the parameters β_{101} , β_{111} and β_{121} where:

$$\beta_{101} = [\text{LnL}]/[\text{Ln}][\text{L}]$$

$$K_1^{\text{H}} = [\text{LnHL}]/[\text{LnL}][\text{H}]$$

and

$$K_2^{\text{H}} = [\text{LnH}_2\text{L}]/[\text{LnHL}][\text{H}]$$

The enthalpies were calculated from the calorimetric titration data as described elsewhere [11]. The experimental conditions ensured a majority of LnL complex formation but the calculation model includes LnL, LnHL and LnH₂L complexes. The heats measured in the calorimeter were corrected for dilution and for the heats attributable to the formation/dissociation of species other than LnL at each titration point.

Results

The acid association constants pK₁ and pK₂ were calculated to be 10.24 ± 0.04 and 9.27 ± 0.04 respectively at 0.50 M (NaClO₄) ionic strength and 25 °C. The corresponding enthalpies and entropies of protonation are listed in Table VI.

Table I is a typical data set for the determination of stability constants in the metal–ligand systems. Column 3 lists the value of log β_{101} calculated at each titration point. The stability constants for the lanthanide complexes are given in Table II. The error limits for the log β_{101} values and the acid association constants are expressed in terms of 95% confidence limits based upon three or more determinations. For the metal–ligand protonation constants, K₁^H and

TABLE I. Data on Stability Constant of the Sm-TMEDTA System. $C_M^0 = 1.00 \times 10^{-3}$ M; $C_L^0 = 1.00 \times 10^{-3}$ M; Titrant = 0.10 M NaOH; T = 25 °C; $pH_0 = 2.84$; I = 0.50 M (NaClO₄).

| Volume (ml) | pH _c | log β ₁₀₁ |
|-------------|-----------------|----------------------|
| 1.25 | 6.22 | 9.54 |
| 1.28 | 6.29 | 9.56 |
| 1.30 | 6.34 | 9.56 |
| 1.32 | 6.39 | 9.56 |
| 1.35 | 6.46 | 9.56 |
| 1.38 | 6.53 | 9.56 |
| 1.40 | 6.57 | 9.57 |
| 1.42 | 6.62 | 9.55 |
| 1.45 | 6.69 | 9.53 |
| 1.48 | 6.76 | 9.51 |
| 1.50 | 6.80 | 9.50 |
| 1.52 | 6.85 | 9.48 |
| 1.55 | 6.93 | 9.41 |

TABLE II. Summary of Stability Constants of TMEDTA Systems*. T = 25 °C; I = 0.50 M (NaClO₄).

| Metal | log β ₁₀₁ | log K ₁ ^H | log K ₂ ^H |
|-------|----------------------|---------------------------------|---------------------------------|
| Sm | 9.52 ± 0.03 | 6.92 ± 0.04 | 5.52 ± 0.08 |
| Eu | 9.83 ± 0.08 | 6.78 ± 0.13 | 5.45 ± 0.20 |
| Gd | 9.94 ± 0.15 | 6.66 ± 0.21 | 5.36 ± 0.26 |
| Tb | 10.41 ± 0.10 | 6.47 ± 0.14 | 5.24 ± 0.18 |
| Dy | 10.55 ± 0.10 | 6.40 ± 0.14 | 5.16 ± 0.18 |
| Ho | 10.84 ± 0.05 | 6.25 ± 0.06 | 5.01 ± 0.10 |
| Er | 10.94 ± 0.10 | 6.20 ± 0.15 | 4.98 ± 0.19 |
| Tm | 11.25 ± 0.08 | 6.05 ± 0.13 | 4.85 ± 0.17 |
| Yb | 11.35 ± 0.13 | 5.98 ± 0.19 | 4.88 ± 0.24 |
| Lu | 11.44 ± 0.13 | 5.94 ± 0.19 | 4.76 ± 0.24 |
| Y | 10.11 ± 0.08 | 6.63 ± 0.13 | 5.48 ± 0.17 |
| Ca | 5.18 ± 0.20 | 8.67 ± 0.26 | 7.45 ± 0.30 |

K₂^H, the determinate errors were estimated, and from the theory of compounding errors [14] a new set of error limits were obtained.

Tables III and IV are the data used for determination of the enthalpies of formation of CaL and protonation of CaL, respectively. The Q values are corrected for dilution effects and heats due to a difference in titrant temperature and cup temperature. The total correction was on the order of +32 mJ per 0.2 ml of titrant added. The standard error for the heats of dilution was ±2 mJ.

Table V presents a typical set of data for the titration for samarium. The Q value is the heat attributable to the formation of the Sm[TMEDTA] species. The error limits are expressed in terms of 95% confidence limits considering each addition of titrant to be one determination and incorporates

TABLE III. Data for Enthalpy of Formation of Ca-TMEDTA Complex. $C_L^0 = 1.00 \times 10^{-1}$ M; $C_H^0 = 1.077 \times 10^{-2}$ M; V₀ = 50.00 ml; T = 25 °C; I = 0.50 M (NaClO₄); Titrant = 0.100 M Ca(ClO₄)₂.

| Volume (ml) | -Q _{corr,dil} (mJ) | ΔH (kJ mol ⁻¹) |
|-------------|-----------------------------|----------------------------|
| 0.20 | — | — |
| 0.40 | 26.08 | 1.74 |
| 0.60 | 25.10 | 1.69 |
| 0.80 | 28.10 | 1.85 |
| 1.00 | 31.80 | 2.04 |
| 1.20 | 23.40 | 1.62 |
| 1.40 | 24.90 | 1.70 |
| 1.60 | 21.80 | 1.54 |
| 1.80 | 19.50 | 1.43 |
| 2.00 | 25.60 | 1.74 |
| 2.20 | 21.50 | 1.54 |
| 2.40 | 18.10 | 1.37 |
| 2.60 | 26.60 | 1.80 |

$$\Delta H_{101} = 1.67 \pm 0.12 \text{ kJ mol}^{-1}.$$

TABLE IV. Data for Enthalpy of Protonation of Ca-[TMEDTA] Complex. $C_L^0 = 1.00 \times 10^{-2}$ M; $C_{Ca}^0 = 1.00 \times 10^{-2}$ M; T = 25 °C; I = 0.50 M (NaClO₄); Titrant = 0.1039 M HClO₄.

| Volume | CaHL (mmol formed) × 100 | Q _{corr,dil} (mJ) | -ΔH (kJ mol ⁻¹) |
|--------|--------------------------|----------------------------|-----------------------------|
| 0.20 | 2.078 | 604.88 | 29.11 |
| 0.40 | 2.078 | 605.18 | 29.12 |
| 0.60 | 2.078 | 591.94 | 28.49 |
| 0.80 | 2.078 | 606.69 | 29.20 |
| 1.00 | 2.078 | 575.01 | 27.67 |
| 1.20 | 2.078 | 582.23 | 28.02 |
| 1.40 | 2.078 | 583.37 | 28.07 |
| 1.60 | 2.078 | 584.19 | 28.11 |
| 1.80 | 2.078 | 561.62 | 27.03 |
| 2.00 | 2.078 | 569.14 | 27.39 |

$$\Delta H = -28.22 \pm 0.54 \text{ kJ mol}^{-1}.$$

data from replicate determinations. A summary of the thermodynamic parameters determined is provided in Table VI.

Discussion

Figures 1–3 compare the values of the free energies, enthalpies and entropies of formation of the 1:1 complexes of trivalent lanthanides and ethylenediaminetetraacetate (EDTA), hydroxyethylenediaminetriacetate (HEDTA), nitrilotriacetate (NTA), and TMEDTA in an ionic strength of 0.50 M (NaClO₄). Also included are the values for the 1:2

TABLE V. Data for Enthalpy of Formation of Sm[TMEDTA] Complex. $C_L^0 = 1.00 \times 10^{-2}$ M; $C_{Ca}^0 = 1.00 \times 10^{-2}$ M; $T = 25$ °C; $I = 0.50$ M (NaClO₄); Titrant = 0.0192 M Sm(ClO₄)₃.

| Volume (ml) | pH _c | [LnL] (mol l ⁻¹) × 10 ⁻⁴ | -Q _{corr,dil} (mJ) | -Q (mJ) | ΔH (kJ mol ⁻¹) |
|-------------|-----------------|---|-----------------------------|---------|----------------------------|
| 0.00 | 8.50 | 0 | — | — | — |
| 0.20 | 8.49 | 0.76 | 121.35 | 109.63 | 28.55 |
| 0.40 | 8.47 | 1.524 | 115.73 | 105.29 | 27.42 |
| 0.60 | 8.46 | 2.277 | 114.16 | 102.93 | 26.81 |
| 0.80 | 8.44 | 3.023 | 111.22 | 99.21 | 25.84 |
| 1.00 | 8.43 | 3.765 | 122.14 | 109.35 | 28.48 |
| 1.20 | 8.41 | 4.500 | 117.98 | 102.13 | 26.60 |
| 1.40 | 8.40 | 5.229 | 121.44 | 107.12 | 27.90 |
| 1.60 | 8.38 | 5.953 | 121.96 | 102.16 | 26.61 |
| 1.80 | 8.37 | 6.671 | 119.00 | 103.16 | 26.87 |
| 2.00 | 8.35 | 7.384 | 124.12 | 102.72 | 26.75 |

$$\Delta H = 27.18 \pm 0.63 \text{ kJ mol}^{-1}.$$

TABLE VI. Summary of Thermodynamic Parameters for TMEDTA Systems. $T = 25$ °C; $I = 0.50$ M (NaClO₄).

| | ΔH (kJ mol ⁻¹) | ΔG (kJ mol ⁻¹) | ΔS (J mol ⁻¹ K ⁻¹) |
|---------------------------|----------------------------|----------------------------|---|
| H + L = HL | -29.49 ± 0.27 | -58.45 ± 0.23 | 97 ± 1 |
| 2H + L = H ₂ L | -57.44 ± 0.37 | -111.36 ± 0.32 | 181 ± 2 |
| H + HL = H ₂ L | -27.97 ± 0.25 | -52.91 ± 0.23 | 84 ± 1 |
| Ca + L = CaL | 1.67 ± 0.12 | -29.57 ± 1.14 | 105 ± 4 |
| CaL + H = CAHL | -28.22 ± 0.54 | -49.49 ± 1.48 | 71 ± 5 |
| Sm + L = SmL | +27.18 ± 0.63 | -54.34 ± 0.17 | 273 ± 2 |
| Eu + L = EuL | +24.78 ± 1.68 | -56.11 ± 0.46 | 271 ± 6 |
| Gd + L = GdL | +24.34 ± 0.99 | -56.74 ± 0.86 | 272 ± 4 |
| Tb + L = TbL | +28.57 ± 1.25 | -59.42 ± 0.57 | 295 ± 5 |
| Dy + L = DyL | +28.42 ± 0.81 | -60.22 ± 0.57 | 297 ± 3 |
| Ho + L = HoL | +24.72 ± 2.01 | -61.87 ± 0.29 | 290 ± 7 |
| Er + L = ErL | +28.04 ± 1.87 | -62.44 ± 0.57 | 303 ± 7 |
| Tm + L = TmL | +23.25 ± 0.66 | -64.21 ± 0.46 | 293 ± 3 |
| Yb + L = YbL | +24.30 ± 1.70 | -64.78 ± 0.74 | 299 ± 6 |
| Lu + L = LuL | +27.35 ± 1.53 | -65.30 ± 0.74 | 311 ± 6 |
| Y + L = YL | +23.90 ± 1.71 | -57.71 ± 0.46 | 274 ± 6 |

complexation by dipicolinate (DP) in 0.50 M ionic strength [15]. The decrease in stability with increase in the alkyl chain length between the nitrogens is obvious. Further, from Figs. 2 and 3 we see that the decrease in stability is due to the endothermic values of the enthalpies of complexation for TMDTA and TMEDTA since their entropies are even more positive than those of EDTA complexation.

To understand these relative values, we must compare the thermodynamic values of protonation of these ligands. The values for TMEDTA are listed in Table VI. For EDTA at $I = 0.50$ M (NaClO₄) to form H₂EDTA⁻²_(aq) from EDTA⁻⁴_(aq), $\Delta H = -50$ kJ mol⁻¹ and $\Delta S = 146$ J mol⁻¹ K⁻¹ (we do not include detailed consideration of the TMDTA system because

of the difference in ionic strength). The differences in the ΔH and ΔS values between the EDTA⁻⁴ and TMEDTA⁻⁴ systems indicate that the latter anion becomes more dehydrated upon protonation. For the entropy, the difference of *ca.* 35 J mol⁻¹ K⁻¹ is about the same as that observed in the entropies of EDTA and TMEDTA complexation in Fig. 3. This suggests strongly that the complexation effects a similar, larger dehydration of TMEDTA relative to EDTA as does protonation.

In the earlier publication [2], we demonstrated the existence of a linear correlation between the entropy of 1:1 lanthanide complexation and the number of carboxylate groups in aminocarboxylate ligands. When the value for LnDCTA complexation

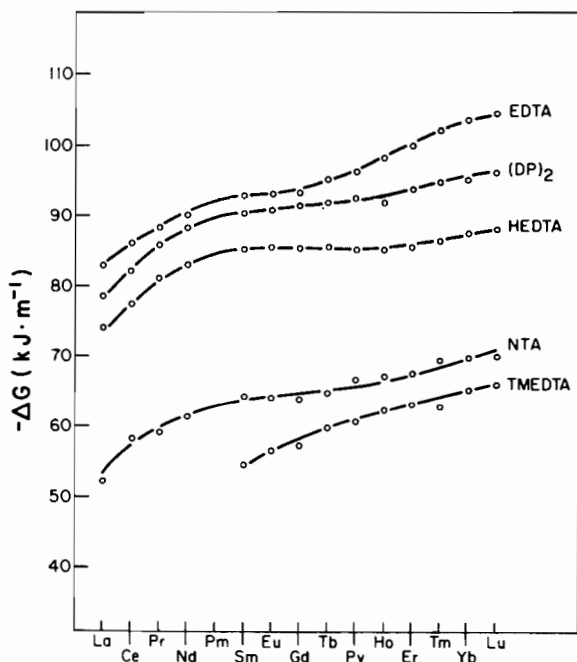


Fig. 1. Comparison of the free energy of complexation in the lanthanide series for some aminopolycarboxylate ligands.

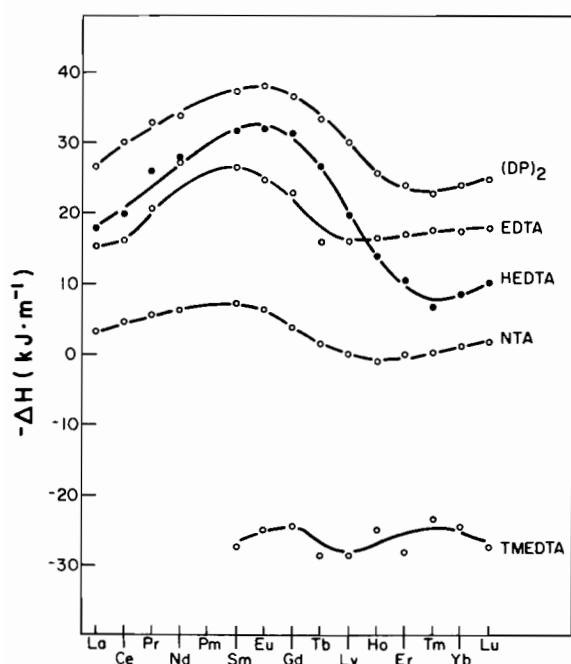


Fig. 2. Comparison of the enthalpy of complexation in the lanthanide series for some aminopolycarboxylate ligands.

was corrected for the extra dehydration of DCTA, it also fitted this correlation. Since the difference in ΔS of LnDCTA and LnEDTA was due to extra dehydration of the DCTA anion, the difference in

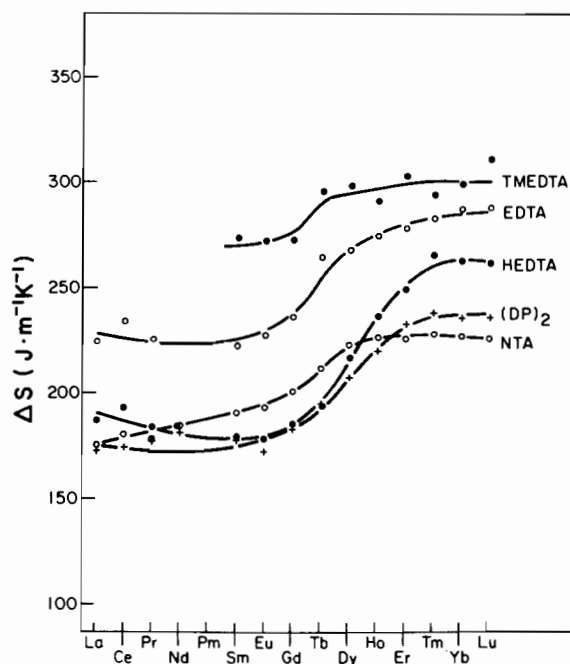


Fig. 3. Comparison of the entropy of complexation in the lanthanide series for some aminopolycarboxylate ligands.

ΔS between LnEDTA and LnTMEDTA is also likely to reflect greater dehydration of the TMEDTA ligand upon complexation.

The previous paper [2] also proposed that the enthalpy of complexation could be adjusted for the lanthanide-carboxylate binding by subtracting four times the enthalpy of lanthanide-acetate complexation (6.5 kJ m^{-1}). The residual enthalpy – presumably due to the lanthanide–nitrogen interaction – did have good linear correlation with the basicity of the nitrogens as measured by their pK_a values. By the same treatment, using SmTMEDTA as the test system, we obtain:

$$\delta\Delta H_{\text{Ln-N}} = +27.2 - 4(6.5) = +1 \text{ kJ m}^{-1}$$

From the earlier correlation, for $\Sigma \text{pK}_a(\text{N}) = 10.2 + 9.3 = 19.5$, we would expect a value of $\delta\Delta H_{\text{Sm-N}} \sim -60 \text{ kJ m}^{-1}$. If only a single amino site was bound ($\text{pK}_a(\text{N}) \sim 10$), then $\delta\Delta H_{\text{Sm-N}}$ would be expected to be *ca.* -25 kJ m^{-1} . Since $\delta\Delta H_{\text{Ln-N}} \approx 0$, there would seem to be no interaction between the lanthanide and the nitrogens. However, the extra dehydration (relative to EDTA) would also change the enthalpy. A compensation effect has been found between ΔH and ΔS in the dehydration term of lanthanide complexes [1, 16]. Accordingly, we can correct the enthalpy of complexation of TMEDTA complexes for the extra dehydration using T ($\Delta\Delta S$) $\approx \Delta\Delta H$.

The corrected enthalpy, ΔH^c is given by $\Delta H^c = \Delta H^{\text{exp}} - \Delta\Delta H$. For $\Delta\Delta S = 35 \text{ J K}^{-1}$, $\Delta\Delta H \approx 10 \text{ kJ}$

m^{-1} and $\Delta H^c = \Delta H^{exp} - 10$. For SmTMedTA complexes, ΔH^c has a value of $+17 \text{ kJ m}^{-1}$. Such a value, in turn, leads to $\delta\Delta H_{Sm-N} \sim -9 \text{ kJ m}^{-1}$. Accordingly, we interpret our data to reflect much weaker Ln-N interactions for the $\overline{N-Ln-N}$ ring of 7 members in LnTMedTA than for the 5-membered ring in LnEDTA complexes.

Since the LnTMDTA data was obtained in 0.10 M ionic strength, it cannot be directly compared. However, when the protonation data of TMDTA and EDTA are compared at 0.10 M ionic strength, the TMDTA anion seems to be more hydrated than the EDTA anion and, in fact, comparable to the TMEDTA anion. Using the differences in ΔH and ΔS of SmEDTA in 0.10 M and 0.50 M ionic strength to correct the SmTMDTA data to 0.50 M ionic strength and, again, correcting (-10 kJ m^{-1}) for the extra dehydration enthalpy, we obtain $\delta\Delta H_{Sm-N} \sim -30 \text{ kJ m}^{-1}$ for SmTMDTA. This indicates stronger Ln-N interaction in the 6-membered $\overline{N-Ln-N}$ ring of the TMDTA complexes than in the 7-membered TMEDTA ring, but weaker than in the 5-membered EDTA ring.

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